1   **Revision 1**

2   **Bonding and electronic changes in rhodochrosite at high pressure**

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10   **Abstract**

11   Rhodochrosite ($MnCO_3$) exhibits a series of high pressure transitions between 15 GPa and 30

12   GPa and at 50 GPa at ambient temperature as observed by *in-situ* Raman spectroscopy, X-ray

13   diffraction (XRD), and X-ray emission spectroscopy (XES). A transition is observed to begin at

14   15 GPa and complete at 30 GPa which may be due to a number of possibilities: modifications in

15   the magnetic order, changes in the compression mechanism, and/or a structural transition

16   resulting from disorder. We also observed a first order phase transition of $MnCO_3$ at 50 GPa

17   which is not accompanied by any changes in the electronic spin state. These results highlight the

18   unique behavior of $MnCO_3$ which we found to be quite different from other common carbonates

19   such as siderite, magnesite and calcite.

20   **Keywords**

21   rhodochrosite, deep carbon, Raman spectroscopy, XES, XRD, high pressure, carbonate

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Introduction

Understanding the behavior of carbon-rich phases in Earth's lower mantle is critical for

modeling the global carbon cycle, since the lower mantle is estimated to contain a hundred times

the carbon in our planet's outersphere (Hirschmann, 2006; Dasgupta and Hirschmann, 2010). In

the mantle, carbon is expected to be present as accessory phases (e.g. carbonate minerals,

graphite or diamond) due to its very low solubility in mantle silicate minerals (Keppler et al.,

2003; Shcheka et al., 2006). A number of high-pressure studies have investigated the stability of

carbonates for a large range of compositions: e.g. $CaCO_3$ (Dickens and Bowen, 1970; Ono et al.,

2005, 2007), $MgCO_3$ (Isshiki et al., 2004; Boulard et al., 2011), $FeCO_3$ (Lavina et al., 2009,

2010; Boulard et al., 2012). These studies demonstrate the importance of the nature of the cation

on the structures of high-pressure phases and their pressure-temperature stability field. Mn^{2+} has

a cation size between that of Mg^{2+} and Ca^{2+}, which could make rhodochrosite ($MnCO_3$) a

potential model compound for understanding the differences in the high pressure behaviors of

Mg and Ca carbonates. Mn is also a $3d$ transition metal which can have a variety of valence and

spin states like Fe in $FeCO_3$.

To date, few studies have been conducted on $MnCO_3$ at high pressure. At ambient

conditions, $MnCO_3$ crystallizes in the *R-3c* {note to typesetting, in all instances like this, the

minus sign is an overbar on top of the 3 (or other number)} structure typical of calcite group

carbonates. Santillán and Williams (2004) reported that this structure is stable up to at least 54

GPa using high pressure infrared (IR) spectroscopy and X-ray diffraction (XRD). More recently,

Ono et al. (2007) reported a phase transition at 50 GPa using XRD coupled with *in situ* laser

heating. Here we present results on the high pressure bonding and electronic behavior of $MnCO_3$

46   studied *in-situ* to over 50 GPa using Raman spectroscopy, XRD and X-ray emission

47   spectroscopy (XES).

48

49   **Experimental details**

50   Our starting material was a natural rhodochrosite sample from the Sweet Home Mine,

51   Alma, CO. From electron micro-probe analysis we determined the composition to be very pure,

52    $(Mn_{0.976} Fe_{0.012} Mg_{0.004} Ca_{0.002})CO_3$, with an uncertainty of approximately 1% in the cation

53   concentrations. In the rest of the text we will refer to this sample as $MnCO_3$.

54

55   *Raman Spectroscopy*

56   We collected *in situ* high pressure Raman spectra of $MnCO_3$ using a Renishaw RM1000

57   Raman microscope in the Extreme Environments Laboratory at Stanford University. This system

58   uses a 514 nm laser excitation line and has 4 cm^{-1} spectral resolution and 2 μm spatial resolution.

59   A small single crystal chip of $MnCO_3$ was loaded into a stainless steel gasket with a 120 μm

60   diameter sample chamber into a symmetric diamond anvil cell (DAC) with 300 micron culets.

61   We used silicone oil as the pressure-transmitting medium, and the ruby fluorescence method was

62   used for determining the pressure (Mao et al., 1986). Raman spectra were collected up to 54 GPa

63   with a pressure step of about 2 GPa.

64

65   *X-ray diffraction*

66   Synchrotron XRD spectra were collected *in situ* at the high pressure beamline 12.2.2 of

67   the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). A

68   powdered sample of $MnCO_3$ was loaded into a symmetric DAC between two layers of NaCl and

69   in a Re gasket. NaCl was used as the pressure transmitting medium and its equation of state was

70   used to determine pressure. The sample was compressed at ambient temperature up to 47 GPa.

71   Angle dispersive XRD measurements were collected using a monochromatic incident X-ray

72   beam ($\lambda = 0.6199$ Å) at each step of pressure of ~5 GPa. The diffraction images were integrated

73   with the Fit2D software (Hammersley et al., 1996), and the XRD patterns were then treated with

74   the General Structure Analysis System (GSAS) software package (Larson and Von Dreele, 2004)

75   using the LeBail method to identify the different phases and refine lattice parameters.

76

77   *X-ray Emission Spectroscopy*

78   The XES experiments were carried out at the beamline 16-IDD of the Advanced Photon

79   Source (APS), Argonne National Laboratory (ANL). A powdered sample of $MnCO_3$ was loaded

80   into the DAC sample chamber within a Be gasket. The pressure was measured using the ruby

81   fluorescence method before and after each XES measurement and was found to be stable within

82   about 3 GPa. The XES signal was collected at 90 degrees from the incident X-ray beam through

83   the Be gasket. The Kβ emission line of Mn was scanned from 6450 to 6510 eV with a 0.4 eV

84   step size. XES spectra were collected between 0 and 54.3 GPa with ~5 GPa steps.

85

86   **Results**

87   *Raman Spectroscopy*

88   The Raman spectra showed four main peaks at ~200, 300, 700 and 1100 cm^{-1}, which

89   correspond to four different vibrational modes in the CO_3^{2-} group (Fig. 1). The modes with lower

90   wave numbers correspond to external modes associated with lattice vibrations that cannot be

91   described in terms of molecular units. In first approximation, these modes involve relative

92   motions of the molecular unit CO_3^{2-} in the surrounding lattice: a translational E_g mode at ~201

93   cm^{-1} (T) and a librational E_g mode at ~302 cm^{-1} (L). The higher frequency modes correspond to

94   internal modes which are restricted to vibrations within the CO_3^{2-}: an in-plane asymmetric

95   stretching E_g mode at ~723 cm^{-1} (ν_4) and a symmetric stretching A_{1g} mode at ~1100 cm^{-1} (ν_1).

96   All of the modes systematically increased in frequency with increasing pressure (Table

97   1). The $\delta\ln\nu/\delta P$ was significantly larger for the external Eg modes (Table 1, Fig. 2). In the

98   compression data, we observed an abrupt step in the Raman shift of the ν_1 mode at 15 GPa, and

99   again above 48 GPa where it develops a new higher frequency peak at the expense of the original

100   peak intensity (Figs. 3,4). These discontinuities were less obvious in the decompression data

101   (Fig. 4). The full width half maximum (FWHM) of the ν_1 mode increases from 0 to 15 GPa and

102   drops gradually until approximately 30 GPa, at which point it increases again until nearly 50 GPa

103   (Fig.5).

104

105   ***X-Ray Diffraction***

106   At low pressure the diffraction pattern can be indexed by a combination of NaCl, Re

107   (from the gasket) and $MnCO_3$, with a = 4.78 Å and c = 15.67 Å at 0.8 GPa which is in good

108   agreement with previous work (e.g. Graf, 1961). The XRD patterns taken under compression

109   indicate that the *R-3c* structure is stable up to 15 GPa. The relative axial compressibilities of a/a$_0$,

110   c/c$_0$ and the axial ratio of c/a are shown in Figure 6. As observed in other carbonate series

111   minerals, the *c* axis is much more compressible than the *a* axis leading to a c/a ratio that decrease

112   with pressure (e.g. Lavina et al., 2010). Figure 7 shows the evolution of the *d*-spacing for the

113   three first diffraction peaks (012), (110) and (01-4) {note to typesetting: in all instances like this,

114   the minus sign is an overbar on top of the 4 (or other number)}with pressure. A change in the

115   slope is observed between 15 and 30 GPa, where the *d*-spacings of the (110) and (012)

116   diffraction peaks remain constant at 2.34 and 3.54 Å respectively, while other diffraction peaks

117   such as the (01-4), (113) or (02-2) continue to decrease in *d*-spacing with pressure. Due to this

118   peculiar evolution of the diffraction peak position, the XRD patterns of $MnCO_3$ above 15 GPa

119   cannot be fit to a rhombohedral structure. Above 30 GPa, the *d*-spacings of all of the diffraction

120   peaks decrease with pressure.

121

122   ***X-Ray Emission Spectroscopy***

123   Figure 8 shows the evolution of the Mn Kβ XES spectra with increasing pressure between 0 and

124   54.3 GPa. The Kβ emission spectrum can be divided into a main line $K\beta_{1,3}$ and a satellite line

125   Kβ' which appears at lower energy due to the exchange interaction between the 3*p* core hole and

126   the unfilled 3*d* shell in the final state of the emission process. The energy separation between the

127   satellite and the main line is proportional to the strength of the exchange interaction and the

128   intensity of the satellite peak is proportional to the net spin of the 3*d* shell (e.g. Badro et al.,

129   1999, 2003). Figure 8a shows XES spectra collected at 0 and 54.3 GPa. We did not observe a

130   collapse of this satellite peak intensity, which indicates that the high spin to low spin transition of

131   Mn^{2+} has not occurred up to at least 54 GPa. However, we did notice a reduction of the intensity

132   of the Kβ' shoulder, which is also reflected by the red shift of the $K\beta_{1,3}$ main peak with pressure.

133   Figure 8b shows the evolution of the energy of the main peak $K\beta_{1,3}$ under compression. The

134   energy of the peak $K\beta_{1,3}$ decreases from 6490.4 to 6490.0 eV while going from 0 to 30 GPa,

135   above which no more changes were observed.

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137

138   **Discussion**

139   *High pressure behavior of MnCO$_3$*

140   Our data suggest that MnCO$_3$ undergoes a series of changes at high pressure. MnCO$_3$ in the

141   *R-3c* structure is stable up to 15 GPa. The *a*-axis contracts by 2 % while the *c*-axis shrinks by

142   6.1% between 0.8 and 15.4 GPa. This difference of compressibility between the two axes is also

143   reflected in the Raman measurements. The relative changes in the Raman shift with increasing

144   pressure ($\delta\ln\nu/\delta P$) describe how sensitive a particular vibrational mode is to changes in pressure.

145   Two external modes are the most sensitive to changes of the unit cell in pressure: The L (E$_g$)

146   mode (Raman shift of approximately 300 cm^{-1}), an asymmetric vibration perpendicular to the

147   CO$_3^{2-}$ plane and with the steepest $\delta\ln\nu/\delta P$ of 0.0131 GPa^{-1}, and the T (E$_g$) mode (Raman shift of

148   approximately 200 cm^{-1}), a symmetric vibrational mode which is also sensitive to changes in

149   pressure with a $\delta\ln\nu/\delta P$ of 0.0125 GPa^{-1}. These modes change the most with pressure because

150   they represent vibrations along the *c* axis, which are more sensitive to external pressure than the

151   other modes that are in the (*a,b*) plane. This is in contrast to the internal mode ν_1 (the most

152   prominent Raman mode in carbonates with a ~1100 cm^{-1} Raman shift) which represents an

153   asymmetric stretching of the oxygens around the central carbon ion and the ν_4 mode (Raman

154   shift of ~700 cm^{-1}) which represents an asymmetric stretching of the CO$_3^{2-}$ group with two of the

155   oxygens moving away from each other in the same plane as the CO$_3^{2-}$. Both of these modes are

156   relatively insensitive to pressure with the $\delta\ln\nu/\delta P$ values of the ν_1 and ν_4 modes almost flat at

157   0.0017 and 0.0011 GPa^{-1} respectively.

158   At 15 GPa we see evidence for the beginning of a transition with an abrupt ~10 cm^{-1} step

159   increase in Raman shift of both ν_1 and ν_4 modes, indicating stiffening of the CO$_3^{2-}$ bonds. The

160   FWHM of the ν_1 mode also reaches a maximum (~2.75 cm^{-1}) at this pressure. This transition was

161   also confirmed by the changes in the XRD patterns. Although no new XRD peaks were

162   observed, the XRD patterns can no longer be fitted by the rhombohedral structure. The *d*-spacing

163   of the (110) XRD peak is constant between 15 and 30 GPa, which indicates that the *a* axis does

164   not evolve. Structurally, the *a* parameter is related to the Mn^{2+}-Mn^{2+} distance and the *c* parameter

165   is related to the Mn^{2+}-CO_3^{2-} distance. Therefore, the volume change of the unit cell results from

166   shrinkage of the Mn^{2+}-CO_3^{2-} distance. From 15 to 30 GPa, the Raman spectra and XRD show a

167   linear evolution. The FWHM of the ν_1 Raman mode decreases up to 30 GPa where it reaches its

168   lowest value ($\sim$1.75 cm^{-1}). At $\sim$30 GPa, a small change in slope is observed for the ν_1 mode. A

169   break in the evolution of XRD peak positions with pressure is also observed. Finally, this

170   transition is accompanied by changes in the XES spectra. A continuous evolution in the $K\beta_{1,3}$

171   position and $K\beta'$ intensity is observed from 0 to 30 GPa and ceases above 30 GPa.

172   From these observations, we propose that $MnCO_3$ undergoes a phase transition at 15 GPa

173   that completes at 30 GPa. The rearrangement of the MnO_6 octahedra may be associated with

174   electronic/magnetic changes although not with a high spin to low spin transition, which might be

175   similar to the magnetic transition observed in MnO at 30 GPa (Yoo et al, 2005). The XRD

176   patterns show that this new phase is different from the known high-pressure polymorphs of other

177   carbonates. However, because of the small number of diffraction peaks in the range of *d*-

178   spacings observed, we were not able to solve the structure of this new high-pressure phase.

179   Ono (2007) performed a synchrotron XRD study using a DAC coupled with laser heating and

180   observed that $MnCO_3$ is stable up to approximately 50 GPa, at which point it transforms into the

181   new orthorhombic structure and undergoes a $\sim$5% volume reduction. We were able to observe a

182   similar phase transition at 50 GPa using Raman spectroscopy but at ambient temperatures. While

183   Santillán and Williams (2004) observed no changes in the $MnCO_3$ structure at high pressure

184   using IR- spectroscopy (IR), our Raman spectroscopy study used a smaller step size and was able

185   to detect the discontinuities and anomalies in the vibrational frequency of the carbonate group.

186   *Comparison of $MnCO_3$ to other carbonates*

187   At high pressure, $MnCO_3$ behaves differently from other common carbonates in the

188   lithosphere and mantle. $FeCO_3$ undergoes an isostructural high spin to low spin transition with an

189   associated ~10% volume collapse around 50 GPa, instead of the series of transitions seen in

190    $MnCO_3$ (Lavina et al., 2009; Farfan et al., 2012). At the spin transition, a new lower frequency

191   peak appears in the Raman spectra of the v_1 mode, indicating a relaxation of the CO_3^{2-} in $FeCO_3$,

192   contrasting the behavior of the CO_3^{2-} group in $MnCO_3$. Thus, despite being neighbors in the

193   periodic table and both being $3d$ transition metals, the carbonates for Fe and Mn display very

194   different high-pressure behavior. Reasons for this difference in behavior of Fe^{2+} and Mn^{2+} may

195   include the difference in their ionic radii (Fe^{2+}, has a radius of 0.78 and Mn^{2+} has a radius of

196   0.83) and the difference in their electronic configurations ([Ar]$3d^5$ for Mn^{2+} in rhodochrosite and

197   [Ar]$3d^6$ for Fe^{2+} in siderite). However, even for isoelectronic Mn^{2+} and Fe^{3+}, both with [Ar]$3d^5$

198   electronic configuration, their compounds behave differently under pressure. For example,

199   pressure-induced spin-transition occurs at ~50 GPa for Fe_2O_3 (Badro et al., 1999, 2002; Wang et

200   al., 2010;) as opposed to at ~105 GPa for MnO (Rueff et al., 2005; Yoo et al., 2005). From our

201   XES experiment, Mn^{2+} in $MnCO_3$ shows no evidence for a spin transition up to 54 GPa. It may

202   take higher pressures to induce a spin transition in $MnCO_3$. The five $3d$ valence electrons of

203   Mn^{2+} are able to spread larger in space than those of Fe^{3+} (Mn^{2+} has a larger radius than Fe^{3+} and

204   a lower oxidation state). This would lead to a smaller crystal field splitting energy for Mn^{2+} in

205    $MnCO_3$, which would favor a high spin configuration over a wider pressure range, similar to

206   what occurs in FeO at high pressure (Badro et al., 1999; Pasternak et al., 1997; Ono et al. 2007).

207

208 In $MnCO_3$, the Mn^{2+} radius (0.83 Å) lies between Mg^{2+} (0.72 Å) and Ca^{2+} (1 Å) in

209 carbonates which makes it a potential candidate for understanding the difference in high-pressure

210 phase behavior between Mg and Ca carbonates which are the two most abundant carbonates on

211 the surface of the planet. Several studies have shown that $MgCO_3$ and $CaCO_3$ display different

212 high-pressure behavior. Magnesite is stable up to at least 112 GPa at room temperature (Fiquet et

213 al., 2002; Isshiki et al., 2004; Boulard et al., 2011). Several high-pressure and high-temperature

214 phases have been reported: a monoclinic phase at 82 GPa-2350K (Boulard et al., 2011), an

215 orthorhombic phase above 115 GPa-2200 K (Isshiki et al., 2004) and a pyroxene structure is also

216 predicted by theoritical calculation above 160 GPa (Oganov et al, 2008). In contrast, calcite

217 transforms into aragonite (orthorhombic) above 2 GPa at high temperature (Suito et al., 2001).

218 However, at room temperature, $CaCO_3$ undergoes a series of metastable phase transitions during

219 compression. Calcite transforms into calcite II at 1.5 GPa and calcite II into calcite III at 2.2 GPa

220 (Bridgman, 1939; Singh and Kennedy, 1974; Merrill and Bassett, 1975). The structure of calcite

221 II differs slightly from calcite I by rotation of the CO_3^{2-} planar groups and a small displacement

222 of the Ca^{2+} cations from the adjacent CO_3^{2-} layer (Merrill and Bassett, 1975; Kawano et al.,

223 2009). The calcite II Raman spectrum is very similar to that of calcite with only a few new low

224 intensity peaks. The XRD patterns are also very similar. The structure of calcite III is still under

225 debate, with several structures having been proposed from different studies (Davis, 1964; Merrill

226 and Bassett, 1975; Smyth and Ahrens, 1997; Merlini et al., 2012).

227   A recent study on the solid solution between Mn and Ca carbonate observed

228 transformation of $(Mn,Ca)CO_3$ into calcite II and calcite III structures for $MnCO_3$ contents up to

229 40% (Shi et al., 2012). They show a progressive increase in the pressure of the two phase

230   transitions with increasing $MnCO_3$ content. By extrapolating to 100% of $MnCO_3$ one would

231   expect rhodochrosite to transform into calcite II structure above 19 GPa and into calcite III above

232   26 GPa. In the present study we observed a phase transition at 15 GPa with a structure close to

233   rhodochrosite, which bears some similarities to the calcite-calcite II relationship. However, here

234   we did not observe any new XRD peaks and Raman peaks in $MnCO_3$ at 15 GPa. This could be a

235   result of the expected new peaks being too weak to be observed, or the high-pressure phase

236   structure reported here being different from the calcite II structure.

237   These features could also be interpreted as a change in the compression mechanism.

238   Similar to our observations of the a and c axes shrinkage, Fiquet et al. (1994) reported a change

239   in the slope of the axial compressibilities in $MgCO_3$ at 8 GPa at which point the c axis became

240   more compressible and the a axis less compressible while still maintaining the rhombohedral

241   structure. In this study we also observed that the a axis becomes incompressible as reflected by

242   the position of the XRD (110) reflection being fixed at 2.34 Å. However, in our experiment on

243    $MnCO_3$, the change in axial compressibilities is associated with the loss of R-3c symmetry.

244   In summary, our *in-situ* Raman spectroscopy, XRD, and XES study reveals the intriguing

245   high pressure behavior of $MnCO_3$, and highlights the contrasting behavior between the different

246   carbonate compositions as well as the need for further study to elucidate their complicated high

247   pressure electronic and bonding behavior.

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Acknowledgments

References cited

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272   Badro, J., V. V Struzhkin, J. Shu, R. J. Hemley, and H. Mao (1999) Magnetism in FeO at

273   Megabar Pressures from X-Ray Emission Spectroscopy, Physical Review Letters, 83(20),

274   4101–4104.

275   Badro, J., G. Fiquet, V. Struzhkin, M. Somayazulu, H. Mao, G. Shen, and T. Le Bihan (2002)

276   Nature of the High-Pressure Transition in Fe_2O_3 Hematite, Physical Review Letters, 89(20),

277   11–14.

278   Badro, J., G. Fiquet, F. Guyot, J.-P. Rueff, V. V Struzhkin, G. Vankó, and G. Monaco (2003)

279   Iron partitioning in Earth's mantle: toward a deep lower mantle discontinuity., Science

280   (New York, N.Y.), 300(5620), 789–91.Boulard, E., A. Gloter, A. Corgne, D. Antonangeli,

281   and A. Auzende (2011), New host for carbon in the deep Earth, PNAS, 108(13), 5184–

282   5187.

283   Boulard, E., Menguy, N., Auzende, A. L., Benzerara, K., Bureau, H., Antonangeli, D., Corgne,

284   A., Morard, G., Siebert, J., Perrillat, J. P., Guyot, F., Fiquet, G. (2012) Experimental

285   investigation of the stability of Fe-rich carbonates in the lower mantle, Journal of

286   Geophysical Research, 117(B2), 1–15

287   Bridgman, P. W. (1939) The high pressure behavior of miscellaneous minerals, American

288   Journal of Science, 237(1), 7–18.

289   Couture, L. (1947) Etude de spectres de vibrations de monocristaux ioniques, Annales de

290   Physique, 17, 88–122.

291   Dasgupta, R., and M. M. Hirschmann (2010) The deep carbon cycle and melting in Earth's

292   interior, Earth and Planetary Science Letters, 298(1-2), 1–13. Davis, B. L. (1964), X-ray

293   Diffraction Data on two high-pressure phases of calcium carbonate, Science, 145, 489–491.

294   Dickens, B., and S. Bowen (1970) Refinement of the crystal structure of the aragonite phase of

295        $CaCO_3$, Journal of Research of the National Bureau of Standards A. Physics and Chemistry,

296   75A, 27–32.

297   Farfan, G., S. Wang, H. Ma, R. Caracas, and W. L. Mao (2012) Bonding and structural changes

298   in siderite at high pressure, American Mineralogist, 97, 1421-1426.

299   Fiquet, G., F. Guyot, and J. Itié (1994) High-pressure X-ray diffraction study of carbonates   :

300        $MgCO_3$, $CaMg(CO_3)_2$ and $CaCO_3$, American Mineralogist, 79, 15–23.

301   Fiquet, G., F. Guyot, M. Kunz, J. Matas, D. Andrault, and M. Hanfland (2002) Structural

302   refinements of magnesite at very high pressure, American Mineralogist, 87, 1261–1265.

303   Graf, D. L. (1961) Crystallographic tables for the rhombehedral carbonates, The American

304   Mineralogist, 46, 1283–1316.

305   Hammersley, a. P., S. O. Svensson, M. Hanfland, a. N. Fitch, and D. Hausermann (1996) Two-

306   dimensional detector software: From real detector to idealised image or two-theta scan,

307   High Pressure Research, 14(4-6), 235–248.

308   Hirschmann, M. M. (2006) Water, Melting, and the Deep Earth H_2O Cycle, Annual Review of

309   Earth and Planetary Sciences, 34(1), 629–653. Isshiki, M., T. Irifune, K. Hirose, S. Ono, Y.

310   Ohishi, T. Watanuld, E. Nishibori, M. Takata, and M. Sakata (2004), Stability of magnesite

311   and its high-pressure form in the lowermost mantle, Nature, 427(January), 60–63.

312   Kawano, J., A. Miyake, N. Shimobayashi, and M. Kitamura (2009) Molecular dynamics

313   simulation of the phase transition between calcite and CaCO(3)-II., Journal of physics.

314   Condensed matter   : an Institute of Physics journal, 21(27), 275403.

315   Keppler, H., M. Wiedenbeck, and S. S. Shcheka (2003) Carbon solubility in olivine and the

316   mode of carbon storage in the Earth's mantle, 424, 414–416.

317   Larson, A. C., and R. B. Von Dreele (2004) General Structure Analysis System (GSAS), Los

318   Alamos National Laboratory Report LAUR, 86–748.

319   Lavina, B., P. Dera, R. T. Downs, V. Prakapenka, M. Rivers, S. Sutton, and M. Nicol (2009)

320   Siderite at lower mantle conditions and the effects of the pressure-induced spin-pairing

321   transition, Geophysical Research Letters, 36(23), L23306.

322   Lavina, B., P. Dera, R. Downs, W. Yang, S. Sinogeikin, Y. Meng, G. Shen, and D. Schiferl

323   (2010), Structure of siderite FeCO_{3} to 56 GPa and hysteresis of its spin-pairing

324   transition, Physical Review B, 82(6), 064110.

325   Mao, H. K., J. Xu, and P. M. Bell (1986) Calibration of the Ruby Pressure Gauge to 800 kbar

326   under quasi-hydrostatic Conditions, Journal of Geophysical Research, 91(B5), 4673–4676.

327   Merlini, M., M. Hanfland, and W. a. Crichton (2012) CaCO$_3$-III and CaCO$_3$-VI, high-pressure

328   polymorphs of calcite: Possible host structures for carbon in the Earth's mantle, Earth and

329   Planetary Science Letters, 333-334, 265–271.

330   Merrill, B. L., and W. A. Bassett (1975) The Crystal Structure of $CaCO_3$ (II), a High-Pressure

331   Metastable Phase of Calcium Carbonate, Acta Crystallographica, B31, 343–349.

332   Oganov, A.R., Ono, S., Ma, Y., Glass, C.W., and Garcia, A. (2008) Novel high-pressure

333   structures of $MgCO_3$, $CaCO_3$ and CO_2 and their role in earth's lower mantle. Earth and

334   Planetary Science Letters, 273, 38–47.

335   Ono, S. (2007) High-pressure phase transformation in $MnCO_3$: a synchrotron XRD study,

336   Mineralogical Magazine, 71(1), 105–111.

337   Ono, S., T. Kikegawa, Y. Ohishi, and J. Tsuchiya (2005) Post-aragonite phase transformation in

338   CaCO3 at 40 GPa, American Mineralogist, 90(4), 667–671.

339   Ono, S., T. Kikegawa, and Y. Ohishi (2007) High-pressure transition of $CaCO_3$, American

340   Mineralogist, 92(7), 1246–1249.

341   Ono, S., Y., Ohishi, and T., Kikegawa (2007) High-pressure study of rhombohedral iron oxide,

342   FeO, at pressures between 41 and 142 GPa, Journal of Physics Condensed Matter, 19(3).

343   DOI:10.1088/0953-8984/19/3/036205.

344   Pasternak, P., Taylor, R., D., Jeanloz, R., Li, X., Nguyen, J. H. and McCammon, C. A. (1997)

345   High Pressure Collapse of Magnetism in $Fe_{0.94}O$: Mössbauer Spectroscopy Beyond 100

346   GPa, Physical Review Letters, 79, 5046–5049.

347   Rueff, J.P., a Mattila, J. Badro, G. Vankó, and a Shukla (2005) Electronic properties of

348   transition-metal oxides under high pressure revealed by x-ray emission spectroscopy,

349   Journal of Physics: Condensed Matter, 17(11), S717–S726.

350   Santillán, J., and Q. Williams (2004) A high-pressure infrared and X-ray study of FeCO3 and

351   MnCO$_3$: comparison with CaMg(CO$_3$)$_2$-dolomite, Physics of the Earth and Planetary

352   Interiors, 143-144, 291–304.

353   Shcheka, S. S., M. Wiedenbeck, D. J. Frost, and H. Keppler (2006) Carbon solubility in mantle

354   minerals, , 245, 730–742.

355   Shi, W., M. E. Fleet, and S. Shieh (2012) High-pressure phase transitions in Ca-Mn carbonates

356   (Ca,Mn)CO$_3$ studied by Raman spectroscopy, American Mineralogist, 97, 999–1001.

357   Singh, A. K., and G. C. Kennedy (1974) Compression of Calcite to 40 kbar, Journal of

358   Geophysical Research, 79(17), 2615–2622.

359   Smyth, J. R., and T. J. Ahrens (1997) The crystal structure of calcite III, Geophysical Research

360   Letters, 24(13), 1595.

361   Suito, K., J. Namba, T. Horikawa, Y. Taniguchi, N. Sakurai, M. Kobayashi, A. Onodera, O.

362   Shimomura, T. Kikegawa, and T. A. K. Ikegawa (2001) Phase relations of CaCO$_3$ at high

363   pressure and high temperature, American Mineralogist, 86, 997–1002.

364   Wang, S. et al. (2010) High-pressure evolution of Fe$_2$O$_3$ electronic structure revealed by x-ray

365   absorption, Physical Review B, 82, 144428.

366   White, W. B. (1974) The carbonate minerals, in The Infrared Spectra of Minerals: Mineralogical

367   Society of London Monograph 4, edited by V. C. Farmer, pp. 227–284.

368   Yoo, C. et al. (2005) First-Order Isostructural Mott Transition in Highly Compressed MnO,

369   Physical Review Letters, 94(11), 115502.

370

371   **Figure captions:**

372

373   Figure 1: Raman spectra of $MnCO_3$ at ambient conditions. The main peaks include two external

374   E_g peaks: a T mode at approximately 201 cm^{-1} and an L mode at approximately 300 cm^{-1} as well

375   as two internal stretching modes: asymmetric stretching ν_4 mode at 700 cm^{-1} and the symmetric

376   stretching ν_1 mode at approximately 1100 cm^{-1}.

377

378   Figure 2: Peak positions for the main Eg modes (T, L and ν_4) modes with increasing pressure.

379   The two vertical dashed lines indicate the range over which the 15-30 GPa transition was

380   observed.

381

382   Figure 3: Raman spectra of the ν_1 mode with increasing pressure. A new higher-frequency peak

383   starts to emerge at 48.2 GPa. The intensity of this new peak increases with increasing pressure at

384   the expense of the original peak.

385

386   Figure 4: Peak positions of the ν_1 mode with increasing pressure. The increasing pressure data

387   cycle is shown as filled circles and the releasing pressure cycle is shown as open circles. The

388   data uncertainties fall within the size of the markers. The dashed line at ~15 GPa outlines a break

389   in the slope in the increasing pressure data, which represents the beginning of a first phase

390   transformation which is completed at ~30 GPa (second dashed line).The peak splitting occurs at

391   around 48 GPa (outlined in a dashed line).

392

393   .

394

395   Figure 5: FWHM of the ν_1, ν_4, and T modes with increasing pressure to 50 GPa.

396

397   Figure 6: The relative axial compressibilities of a/a$_0$ (black squares), c/c$_0$ (open squares) and the

398   axial ratio of c/a (black dots) for the rhombohedral phase ofMnCO$_3$ as a function of pressure.

399   Error on the lattice parameter from GSAS refinements fall within the symbols size.

400

401   Figure 7: XRD patterns collected at room temperature. Left: XRD pattern at 0.1 GPa, (hkl) of the

402   rhodochrosite peaks are indexed. Right: evolution of the *d*-spacing of these diffraction peaks.

403

404   Figure 8: a) XES collected at 0 (open squares) and 54.3 GPa (black circles). The intensities are

405   normalized so the maximum intensity of the main peak is 1. b) Energy of the main peak K$\beta_{1,3}$

406   with the pressure.

407

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410
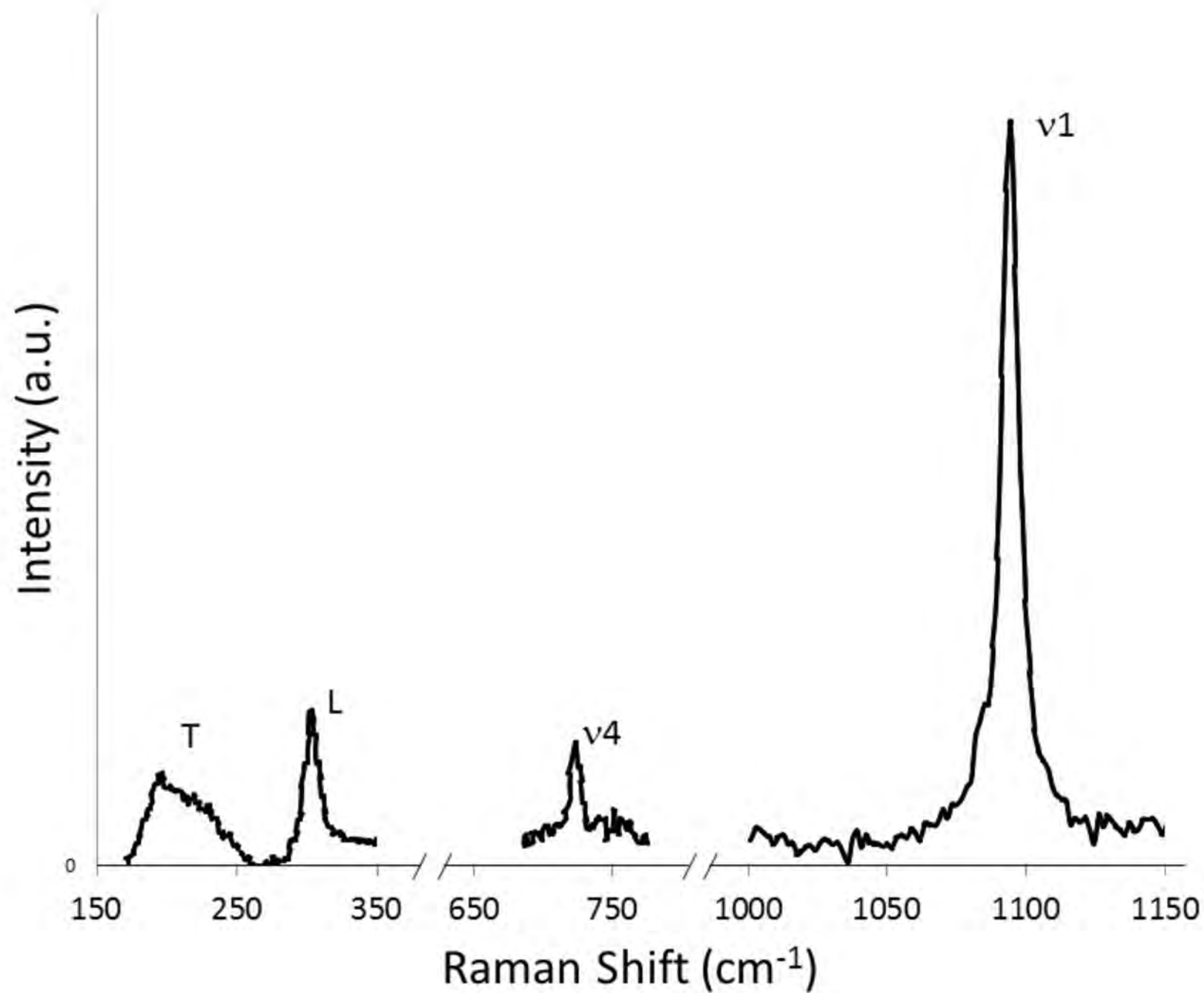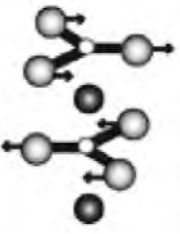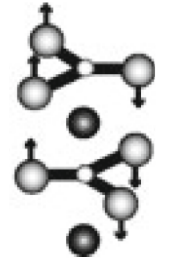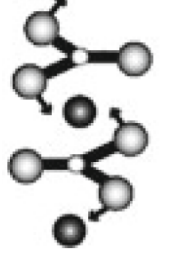
Figure 1

Table 1: Pressure dependence of Raman modes in $MnCO_3$.

Raman mode*	Frequency at ambient conditions (cm^{-1})	$\delta v/\delta P$ (cm^{-1}/GPa)	$\delta \ln v/\delta P$ (GPa^{-1})	Schematic of Raman modes (Boulard et al., 2012)
E_g (T) external symmetric vibration	201	2.685	0.0125	
E_g (L) external asymmetric vibration	302	4.147	0.0131	
E_g (v_4) internal asymmetric C-O stretching	723	0.946	0.0011	
A_{1g} (v_1) internal symmetric C-O stretching	1100	1.906	0.0017	
v_1 split	split peak at 48 GPa	2.339	0.0022	

* Raman group assignments from Couture (1947) and White (1974).

Figure 2

55.2 GPa

51.7 GPa

48.2 GPa

37.0 GPa

25.9 GPa

15.0 GPa

3.3 GPa

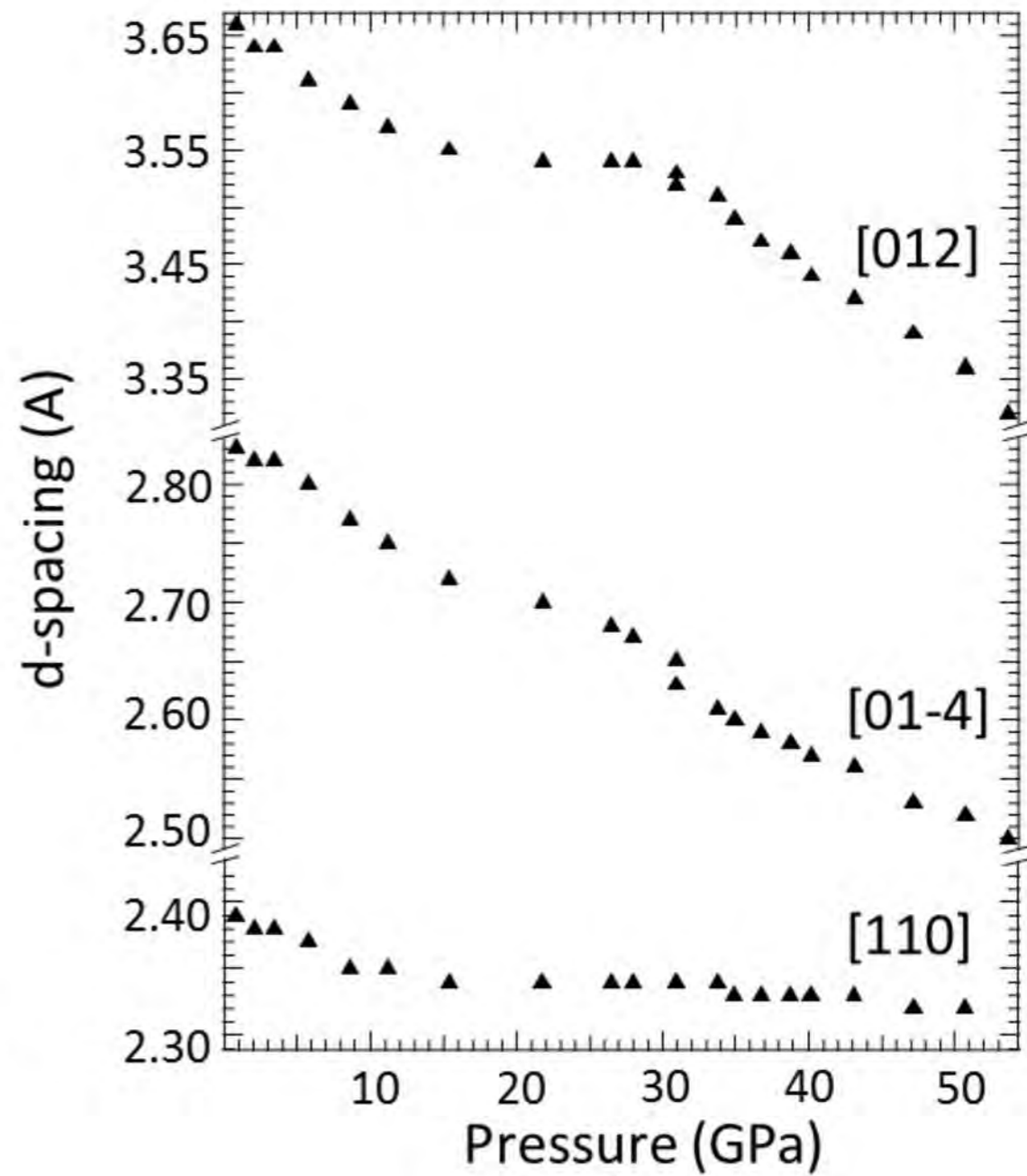1050   1150   1250

Raman Shift (cm^{-1})
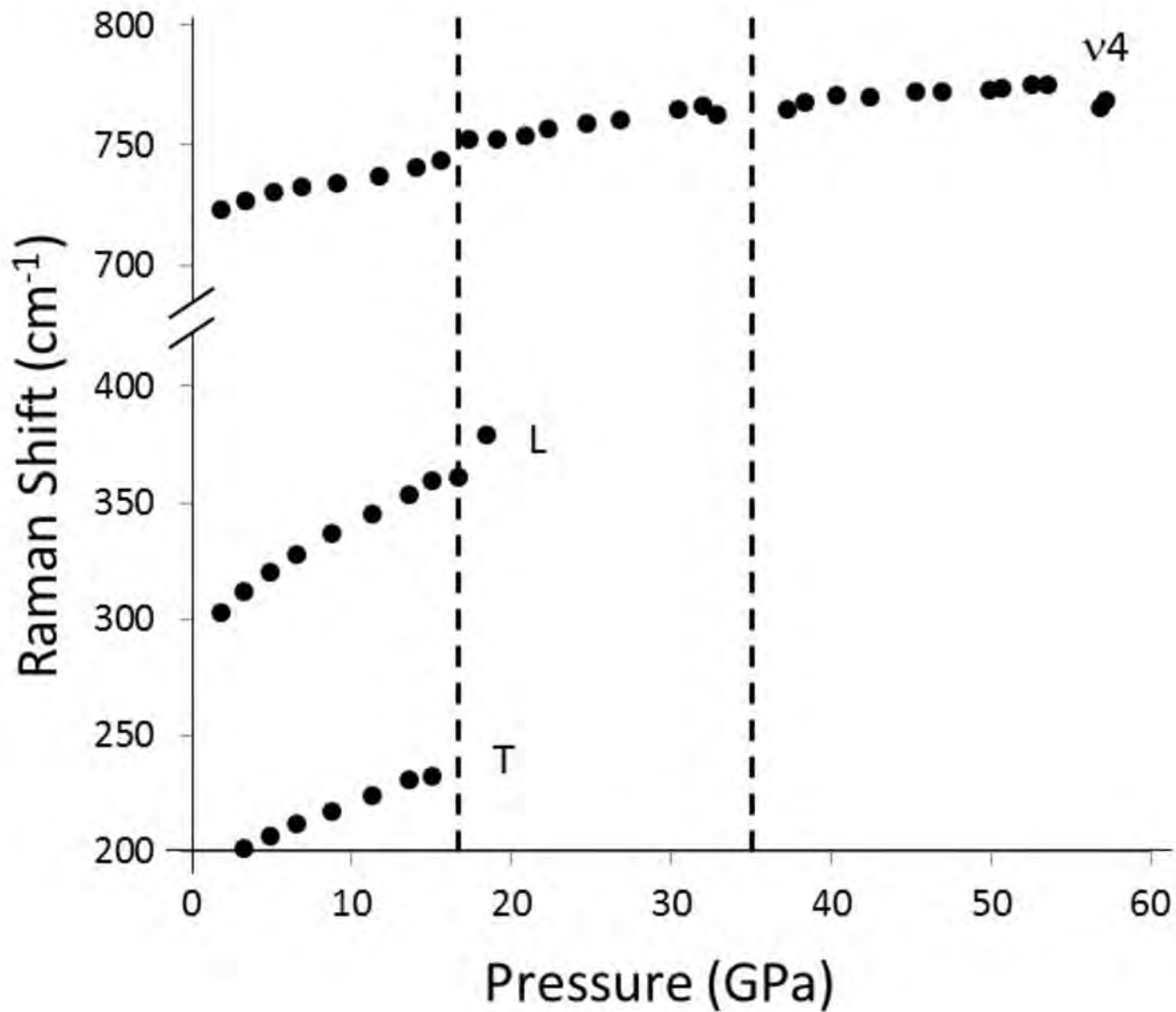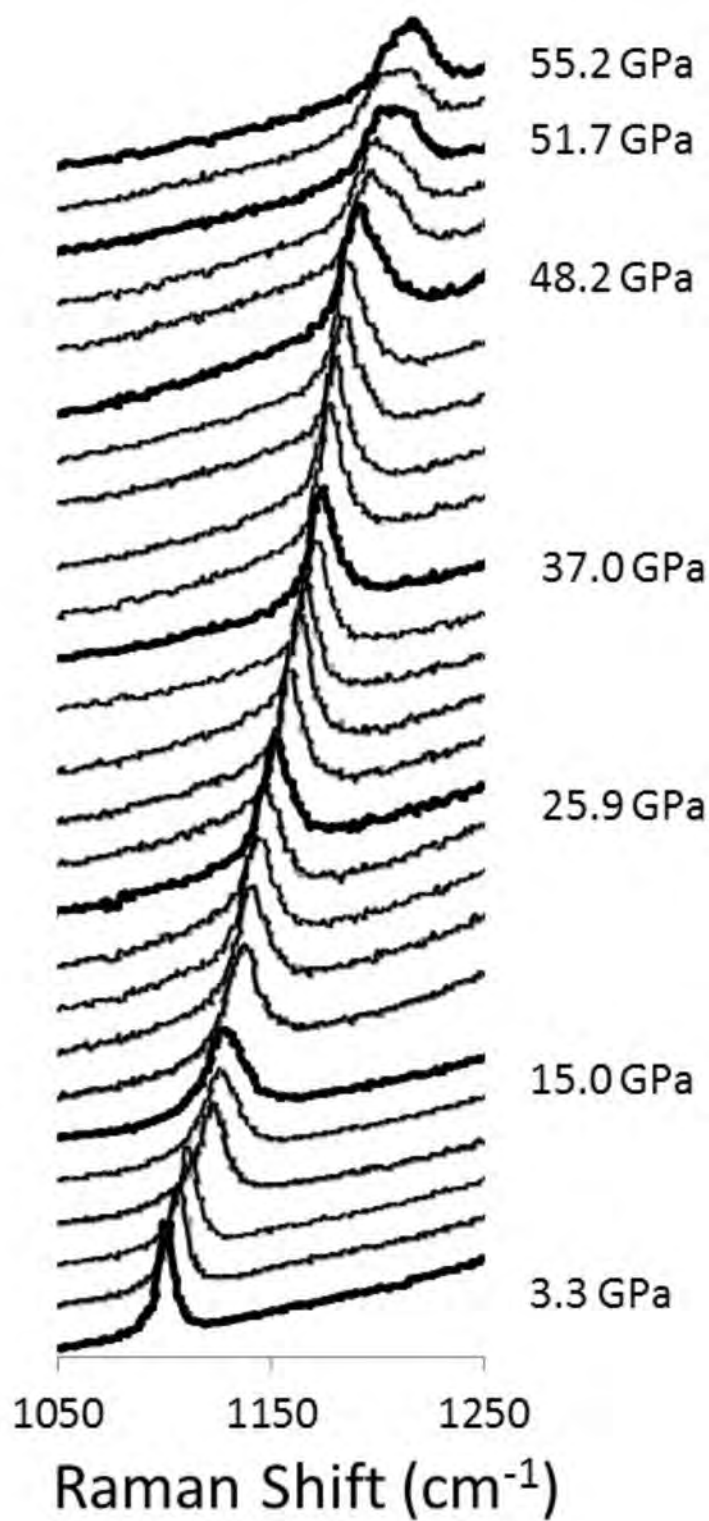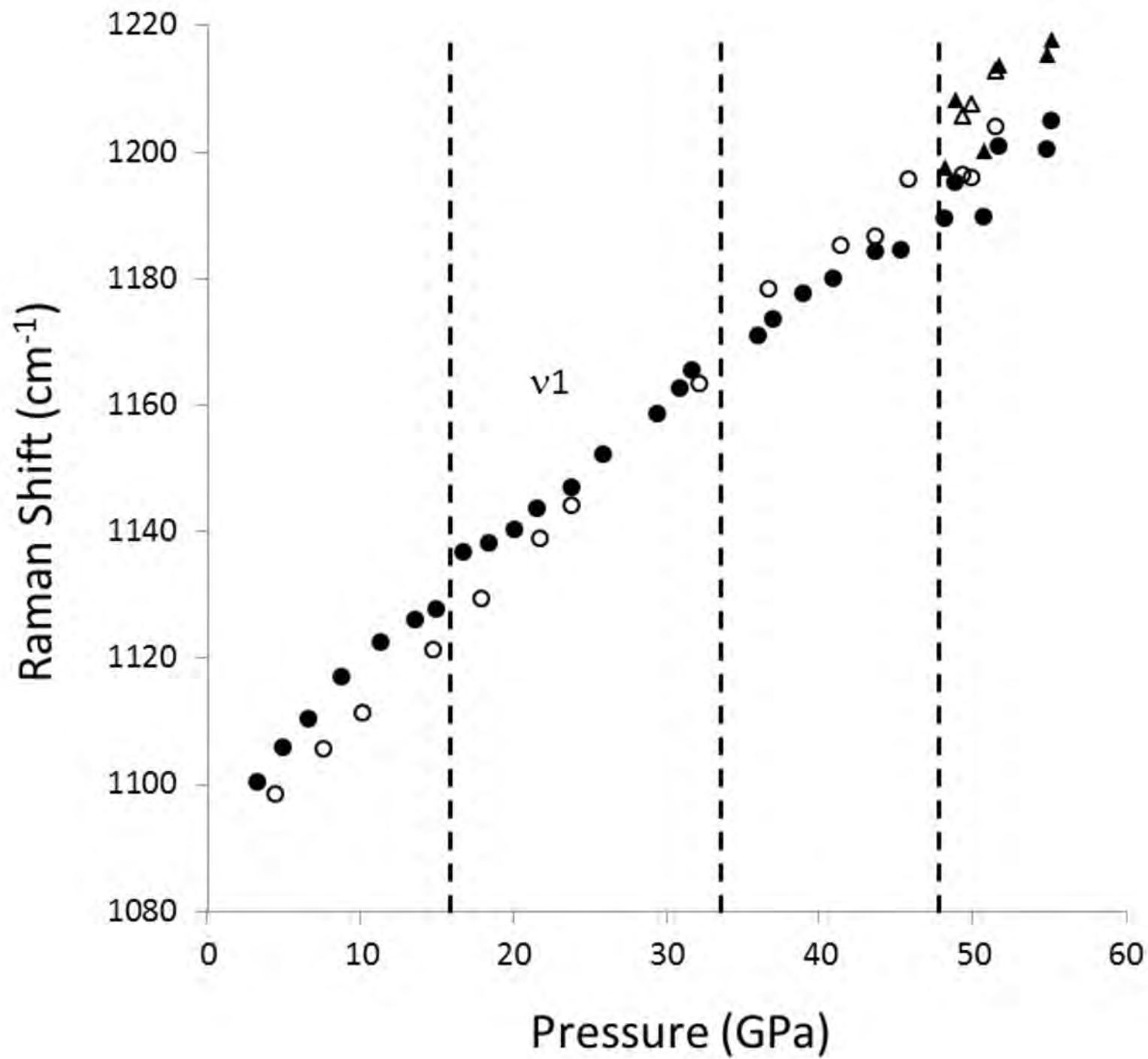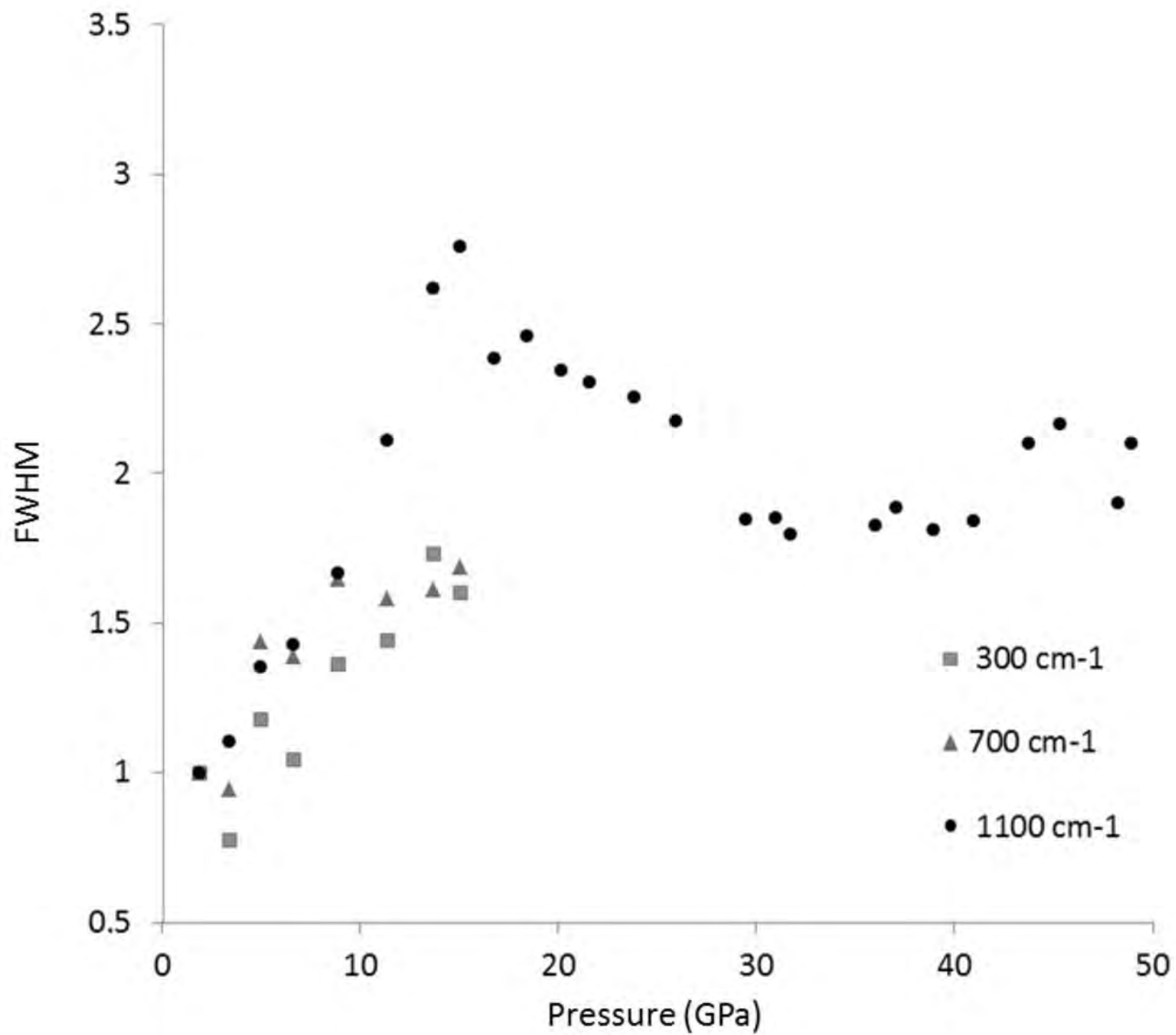
Figure 3

Figure 4

Figure 5
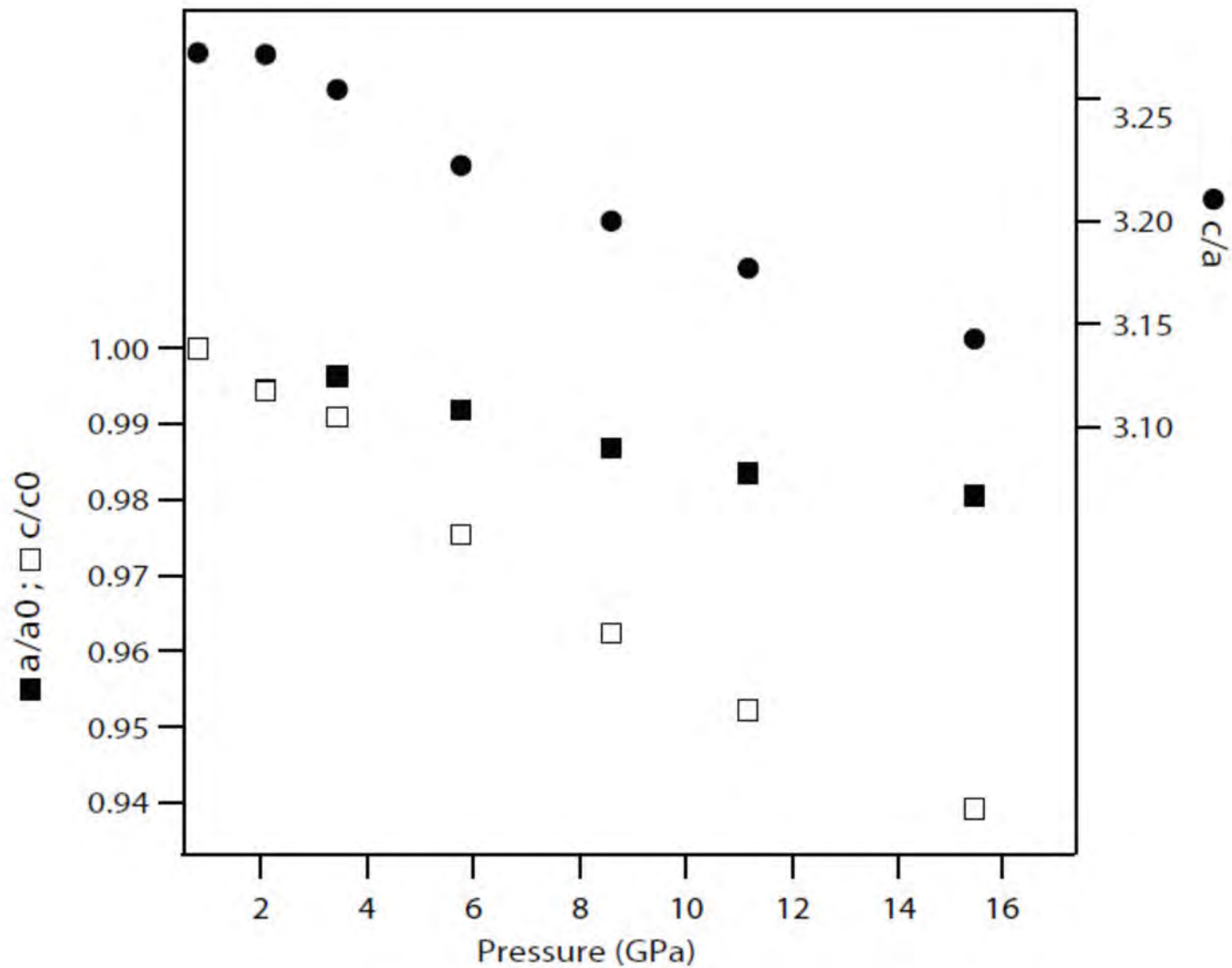
Figure 6

Figure 7

Figure 8